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CHARACTERISTICS OF REACTOR FUEL PROCESS WASTES

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The various types of high-level radioactive liquid wastes currently produced as effluents from reactor fuel processing plants are reviewed. Wastes expected from processes under development for power reactor fuels are also discussed. The wastes are characterized according to their chemical compositions, physical properties, and fission product activity levels.

This paper indicates the types and characteristics of the highly radioactive liquid wastes resulting from chemical processing of current and anticipated irradiated reactor fuels. Wastes containing only very small amounts of fission products, including certain gaseous wastes, may be released to the environment. However, the large volumes of radiochemical wastes of immediate concern contain large amounts of fission products and cannot be released to the environment because of the biological hazards. Unlike conventional industrial wastes and sewage, which may be rendered biologically harmless and then released, radiochemical wastes cannot be made less radiotoxic by any known treatment, and the practice has been to store the concentrated fission product solutions in large tanks interred at the surface of the earth. However, the growth of a nuclear power economy will involve increasing volumes of radioactive wastes, and such storage will become prohibitively hazardous.

First-hand familiarity with these wastes has until recently been limited to persons actively engaged in atomic energy operations. However, it has become increasingly evident that the assistance of specialists from many other fields of science and technology will be required before suitable methods for ultimate disposal can be developed and evaluated. The information given here is intended to introduce the disposal problems to interested persons in related fields.

Origin of Wastes

Irradiated reactor fuels are chemically processed to reclaim the unburned nuclear fuel and recover the transmutation products, such as Pu^{239} or U^{233} , from mixtures of the fission products and inert components of the fuel. At the present time, these are separated by solvent extraction (Fig. 1). While the processing details vary with the fuel being processed and the plant performing the operation, the basic principles are the same. Solid fuels, which have been stored 90-120 days following removal from the reactor (to permit decay of short-lived fission product activities), are dissolved in nitric acid, and the solution is fed to the mid-section of an extraction column where it is contacted with an immiscible organic solvent that enters at the bottom. The solvent selectively extracts the uranium and plutonium; and an aqueous salt solution, added to the top of the column, scrubs the traces of fission products from the organic extract before it leaves the top of the column. The waste, containing more than 99.9% of the dissolved fission products, and inerts in the feed and scrub solutions, leaves at the bottom of the column. The uranium and plutonium are separated from each other and decontaminated further from fission products by additional treatment; but the waste from these steps contains very small amounts of activity and, in some cases, it recycled to the process.

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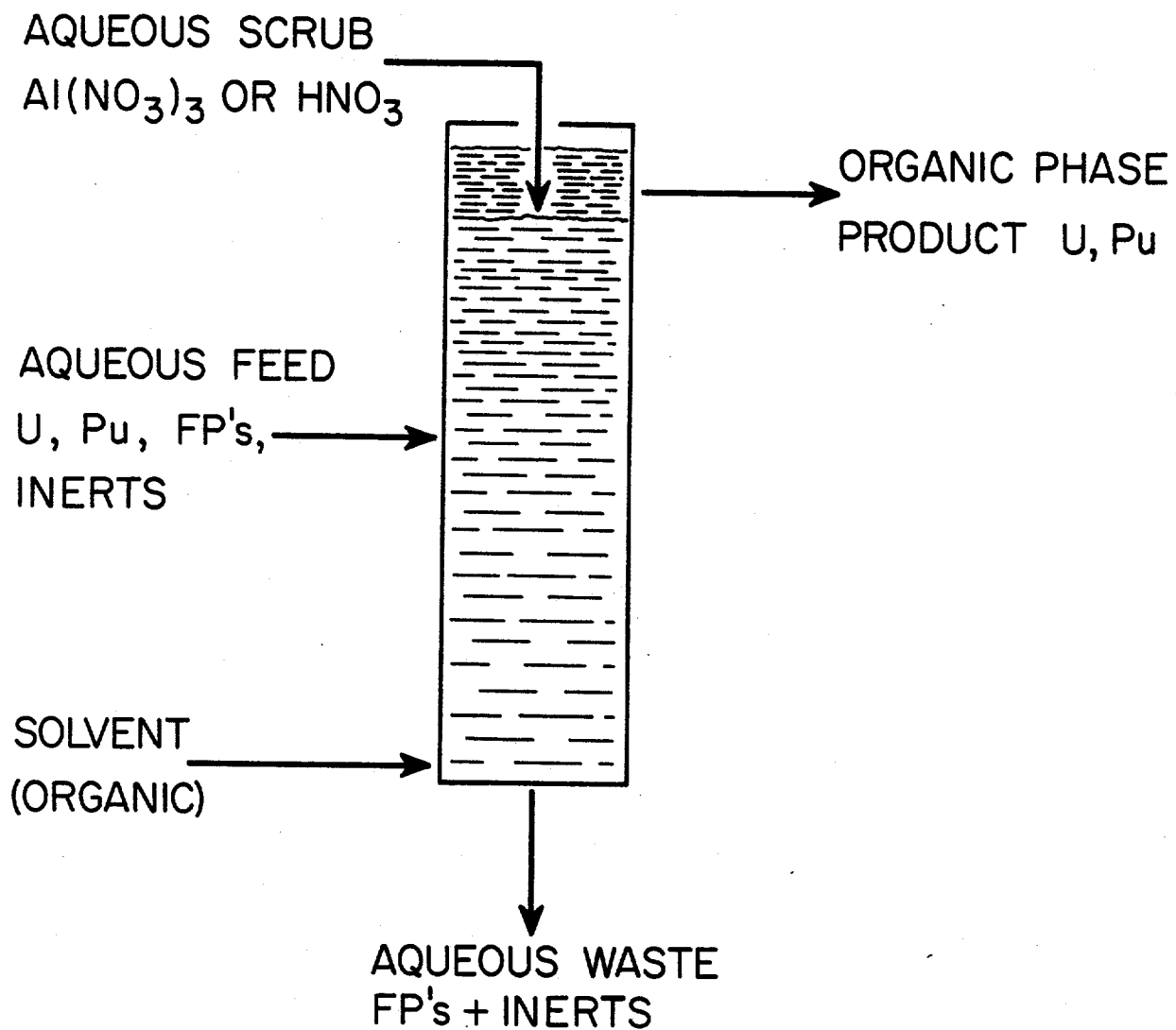


FIG.1. SOLVENT EXTRACTION SEPARATION COLUMN

Several processes in current use for processing irradiated fuels are shown in Table 1. It should be noted that the volumes given refer to the wastes as they come from the extraction column. In current practice, the wastes are evaporated to smaller volumes and are frequently neutralized before being stored in underground steel and concrete tanks.

Table 1. Characteristics of Solvent Extraction Processes

<u>Process</u>	<u>Application</u>	<u>Solvent</u>	<u>Salting Agent</u>	<u>Approx. Vol. Untreated High-activity Waste</u>
Purex	{ Pu-natural Uranium	TBP in hydrocarbon	HNO_3	990 gal/metric ton U
Redox		Hexone	$\text{Al}(\text{NO}_3)_3$	1000 gal/metric ton U
Hexone-25	{ Enriched U-Al alloys	Hexone	$\text{Al}(\text{NO}_3)_3$	700 liters/kg enriched U
TBP-25		TBP in hydrocarbon	$\text{HNO}_3 + -$ $\text{Al}(\text{NO}_3)_3$	670 liters/kg enriched U
Thorex	Th-U ²³³	TBP in hydrocarbon	$\text{Al}(\text{NO}_3)_3$	1360 gal/metric ton Th

Characteristics of Present Wastes

Three types of irradiated fuels are currently being processed: (1) natural uranium, where plutonium and uranium are separated from fission products and from each other; (2) uranium-235 - aluminum alloys where uranium-235 is recovered and separated from fission products; and (3) thorium, where uranium-233 and thorium are separated from fission products and each other. In each process the fuel is dissolved with nitric acid solutions, in preparation for the subsequent liquid-liquid extraction step. The solvents used for extraction are tributyl phosphate (TBP) or methyl isobutyl ketone (hexone). When TBP is used,

it is diluted with a paraffinic hydrocarbon in order to obtain more favorable physical characteristics, and nitric acid is usually used as the salting agent in the aqueous scrub. This yields a waste (see below) that can be evaporated to much smaller volumes than is possible when aluminum nitrate is used as a salting agent, as in hexone extractions.

Table II gives the characteristics of the high-activity wastes produced by these processes. It should be emphasized that the numbers given are all approximations, the actual values depending on the operating characteristics of the particular chemical plant and the details of the chemical flowsheet being used. In addition to the concentrations of inert chemicals given here, all the wastes contain fission products and lesser amounts of uranium, plutonium, and other heavy elements. The presence of these heavy elements is attributable mainly to process losses which usually approximate 0.1%.

Purex-type wastes⁽¹⁾ are mainly solutions of fission products in nitric acid and their physical properties are essentially those of about 1 M HNO_3 . Trace constituents are iron, nickel, and chromium, present in varying amounts as products of corrosion of the stainless steel process equipment. Because of their low solids content, these wastes can be concentrated by evaporation to relatively small volumes and much of the nitric acid distilled and recovered for reuse in the process. Purex-type waste can be concentrated to about 8 M HNO_3 , at which point oxidation of the fission product ruthenium to the volatile RuO_4 begins. The waste is then neutralized by addition of 50% NaOH solution and evaporated to near the solubility limit of the dissolved salts.

The wastes from the rest of the processes considered here contain significant amounts of aluminum. In the Redox process,⁽²⁾ aluminum is added as a salting agent. In the processes for enriched uranium, it is present in the feed

Table II. Characteristics of Current High-activity Wastes

<u>Characteristic*</u>	<u>Purex</u>	<u>Redox</u>	<u>Hexone 25</u>	<u>TBP 25</u>	<u>Thorex</u>
H, <u>M</u>	0.93	-0.3	-0.2	1.33	-0.05
Al, <u>M</u>	-	1.08	1.6	1.63	0.62
Na, <u>M</u>	-	0.23	-	-	-
NH ₄ , <u>M</u>	-	-	1.4	-	-
Hg, <u>M</u>	-	-	0.01	0.01	0.01
NO ₃ , <u>M</u>	0.93	3.05	6.0	6.2	1.8
F, <u>M</u>	-	-	-	-	0.039
Cr ₂ O ₇ , <u>M</u>	-	0.06	-	-	-
NH ₂ SO ₃ , <u>M</u>	-	-	-	0.04	-
Fe, Ni, Cr, g/liter	<1	<1	<1	<1	<1
Si, g/liter	-	-	<1	<1	-
PO ₄ , SO ₄	-	-	-	-	<1
Volume untreated	990 gal/ ton U	1000 gal/ ton U	700 liters/ kg U	670 liters/ kg U	1360 gal/ ton Th
Specific gravity	1.03	1.16	1.25	1.25	1.10
Boiling point °C	101	108	105	105	101
Freezing point, °C	-3	-18	-24	-24	-15
Specific heat	0.97	0.78	0.7	0.7	0.85
Vol after evaporation	60 gal/ ton U	490 gal/ ton U	510 liters/ kg U	500 liters/ kg U	380 gal/ ton Th
Vol after neutralization	80 gal/ ton U	830 gal/ ton U	860 liters/ kg U	840 liters/ kg U	640 gal/ ton Th

*Chemical composition is exclusive of fission products and heavy elements.

solution since it is a major component of the original fuel. In the Thorex process, it is used to provide what is known as an "acid deficient" condition, i.e., one in which the aluminum partially hydrolyzes to the monobasic or dibasic nitrates. The acid deficient solution is also used in the Redox and Hexone-25 processes.

The Redox waste contains some sodium, which is added in adjusting the feed solution to an acid deficient condition, and some dichromate, which is used to oxidize the plutonium to an extractable valence state. Ammonia is used to adjust for acid deficiency in the ^{Hexone} TBP-25 process.

The Hexone-25 and TBP-25 wastes ⁽³⁾ have mercury, and the Thorex waste has both mercury and fluoride, which are added as catalysts in dissolving the fuel.

~~Ferrous sulfamate is added in the TBP-25 process scrub solution to reduce plutonium to a nonextractable valence state, thus effecting its separation with the fission products from uranium.~~

The trace constituents in these wastes include iron, nickel, and chromium as products of stainless steel corrosion, and, in some cases, small amounts of silicon and other impurities originally present in the fabricated fuel. Phosphate and sulfate are used in the Thorex process ⁽⁴⁾ to increase the decontamination of specific fission products and remove interfering ions.

The aluminum-bearing wastes are normally evaporated until the aluminum concentration reaches 2.2 M. If neutralization is desired, the pH is adjusted to about 13 by addition of 50% NaOH solution, 25-30% in excess of the stoichiometric amount required to form sodium aluminate.

Wastes from Power Reactor Fuel Processing

As mentioned earlier, it is through the growth of a nuclear power economy that we can expect a large increase in production of radioactive wastes over the

remainder of this century. It is impossible to predict with assurance either the rate and magnitude of growth of such an industry or the characteristics of the wastes to be encountered. However, in order to permit higher reactor operating temperatures and more efficient recovery of heat, the fuels will probably be fabricated of high-melting metals and alloys, such as zirconium, molybdenum, and the stainless steels. Processes for recovery of such fuels are currently under development.

Although both aqueous and pyrochemical processing methods are being studied, it appears that in the immediate future processes will consist of methods for getting the fuels into aqueous solutions which can be processed by solvent extraction in the conventional manner. The application of large-scale non-aqueous or pyrochemical processing methods seem to lie in the more distant future.

As an indication of the aqueous wastes expected, based on current development work, processes for recovery of three types of power reactor fuels are characterized in Table III. For recovery of enriched uranium from zirconium-uranium alloys of high zirconium content, it has been proposed to dissolve the alloy in HF, complex the ~~zirconium~~ and fluoride by addition of aluminum nitrate, then extract with TBP.⁽³⁾

Stainless-steel-enriched uranium fuels can be processed by dissolving the steel with 4-6 M sulfuric acid and then dissolving the uranium in nitric acid.⁽³⁾ The uranium would be extracted from the resulting solution with TBP. The Darex process,⁽⁵⁾ a more recent development, is expected to be applicable to all stainless-steel-containing fuels. The uranium and stainless steel are dissolved in dilute aqua regia, after which the hydrochloric acid is distilled off nearly quantitatively, leaving a solution of stainless steel and uranium in nitric acid. The uranium and plutonium would be recovered by TBP extraction.

Table III. Power Reactor Fuel Recovery Processes

<u>Process</u>	<u>Fuel</u>	<u>Process Description</u>
Aqueous HF--TBP-25	High Zr--enriched U	HF dissolution, F complexing with Al, oxidation of U with Cr_2O_7 , extraction of U with TBP
Sulfuric Acid--TBP-25	Stainless steel-enriched U	H_2SO_4 dissolution of SS, HNO_3 dissolution of U, extraction of U with TBP
Darex--Purex	Stainless steel-natural U	Dilute aqua regia dissolution, distillation of HCl, extraction of U and Pu with TBP

The high-activity wastes to be expected from processes such as these are given in Table IV. In addition to the chemical composition and volumes of untreated waste per unit of uranium processed, estimates are given of specific gravities, boiling and freezing points, specific heats, and viscosities. Because of their corrosivity and the chemical nature of the wastes, it is not certain whether evaporation will be feasible in many cases. Preliminary investigations show that the Darex-type wastes may be concentrated to stainless steel concentrations of 50 to 100 g/liter without resulting in instability. None of the wastes can be neutralized without precipitation of dissolved salts.

Fission Product Levels

Although the fission products are the source of most of the radiation hazard, they do not greatly influence the chemical properties of the wastes because they are present in such low concentrations. For every mega-watt-day of irradiation, about 1.1 g of fission products--both radioactive and stable--is formed. On this basis, it can be seen that most of the untreated wastes contain of the order of 1 g/liter of total fission products, consisting of isotopes of some 37 elements

Table IV. Characteristics of High-Activity Power Reactor Fuel Processing Wastes

<u>Characteristic*</u>	<u>Zirconium-25-TBP</u>	<u>Stainless Steel-25-TBP</u>	<u>Darex SS-28-TBP</u>
H, <u>M</u>	1.0	3.4	2.0
Al, <u>M</u>	0.75	-	-
Zr, <u>M</u>	0.55	-	-
Fe, <u>M</u>	-	0.07	0.18
Cr, <u>M</u>	-	0.02	0.05
Ni, <u>M</u>	-	0.007	0.018
NO ₃ , <u>M</u>	2.3	2.7	2.3
F, <u>M</u>	3.2	-	-
SO ₄ , <u>M</u>	-	0.5	-
Cr ₂ O ₇ , <u>M</u>	0.01	-	-
Fe, Ni, Cr, g/liter	<1	-	-
Cl, g/liter	-	-	<1
Mn, P, Si, g/liter	-	<1	<1
Vol, untreated	330 liters/kg U	330 liters/kg U	1760 gal/ton U
Specific gravity	1.2	1.1	1.2
Boiling point, °C	101	106	107
Freezing point, °C	Metastable < 25°C	-6	-22
Specific heat	-	0.84	0.75
Viscosity, cp	2	1.2	1.3
Vol after evaporation	-	-	300 gal/ton (80 g SS/liter

*Chemical composition is exclusive of fission products and heavy elements

lying between zinc and dysprosium in the periodic table. While the total number of fission product atoms does not change after irradiation, the concentration of specific fission products does change with time, and for any given fuel is a function of the reactor power level during irradiation, the length of time the fuel has been irradiated, and the time elapsed since discharge from the reactor. The estimate of fission product levels and the nuclear properties of fission product mixtures is beyond the scope of this paper, but an extensive correlation of such information for thermal fission of U^{235} has recently been published. (6)

The contribution to the total beta activity by fission products of ten different mass numbers is presented in Figure 2. For the purposes of this illustration, natural uranium irradiated in a thermal neutron flux of 3×10^{13} $n/cm^2/sec$ for one year was chosen as a basis. At a decay time of 10 days, 63 d Zr^{95} and its daughter, 35 d Nb^{95} , account for 20 percent of the total beta activity. They are followed in order of decreasing significance by 12.8 d Ba^{140} and 40 h La^{140} and by 290 d Ce^{144} and its 17.5 m Pr daughter. In the range of 100 to 1000 days decay, 290 d Ce^{144} - 17.5 m Pr^{144} represent 40 to 60 percent of the total activity. After this time, Sr^{90} and Cs^{137} and their daughters begin to assume an increasingly dominant role. In all, the isotopes considered here represent about 63 percent of the total activity after 10 days decay, 87 percent after 100 days decay, and greater than 98 percent at 1000 days and thereafter.

One of the properties of fission product mixtures of most interest to waste disposal is their heat emission. In any disposal scheme, provision must be made to dissipate the heat evolved as a consequence of radioactive decay if elevated temperatures which can lead to chemical instability, corrosion, and entrainment during storage are to be avoided. A typical curve of the fission product power expected in wastes from processing a fuel of high burnup is given in Figure 3.

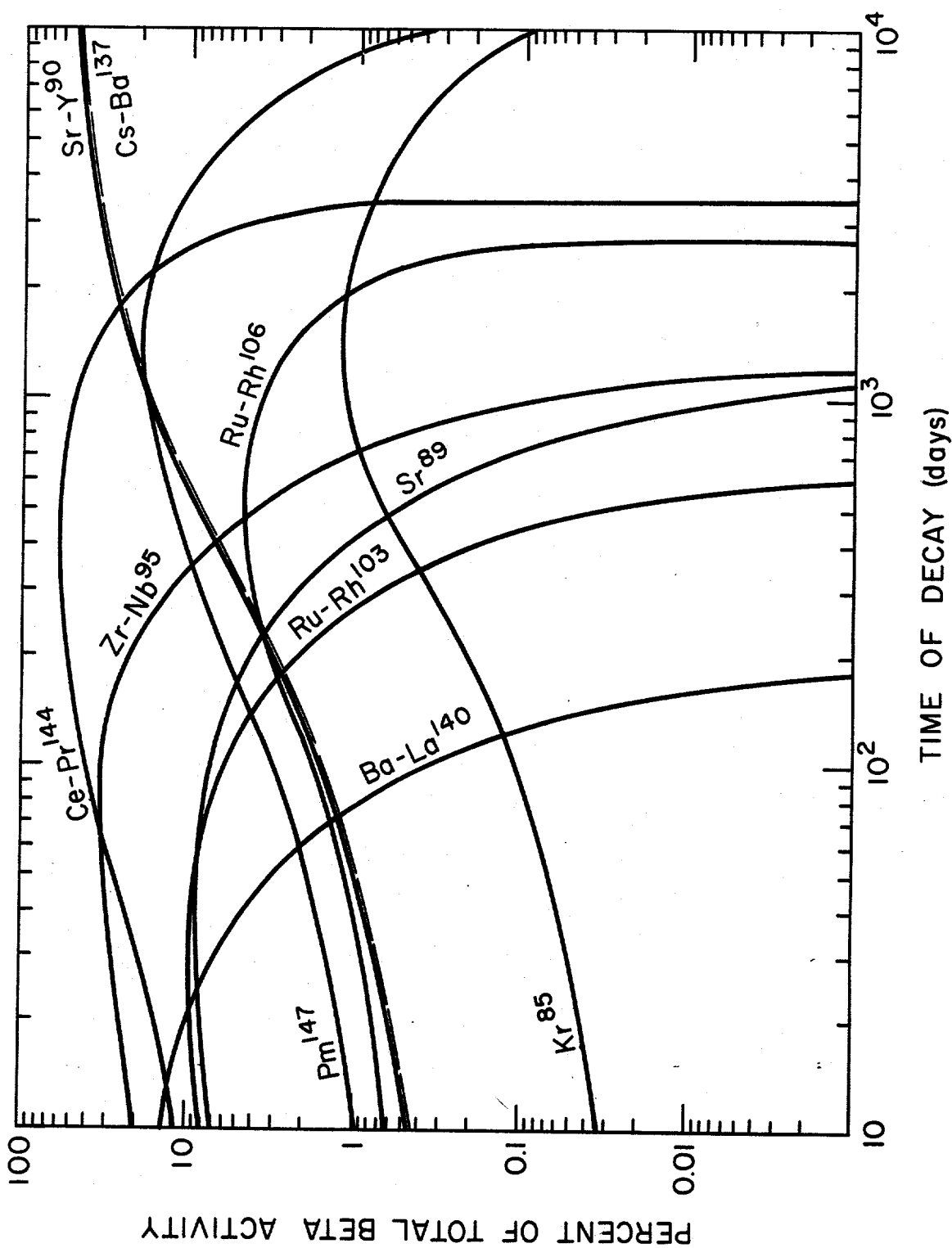


FIGURE 2 DISTRIBUTION OF FISSION PRODUCT ACTIVITY AS A FUNCTION OF DECAY TIME. BASIS: IRRADIATION AT THERMAL FLUX OF 3×10^{13} n/cm²/sec FOR 1 YR.

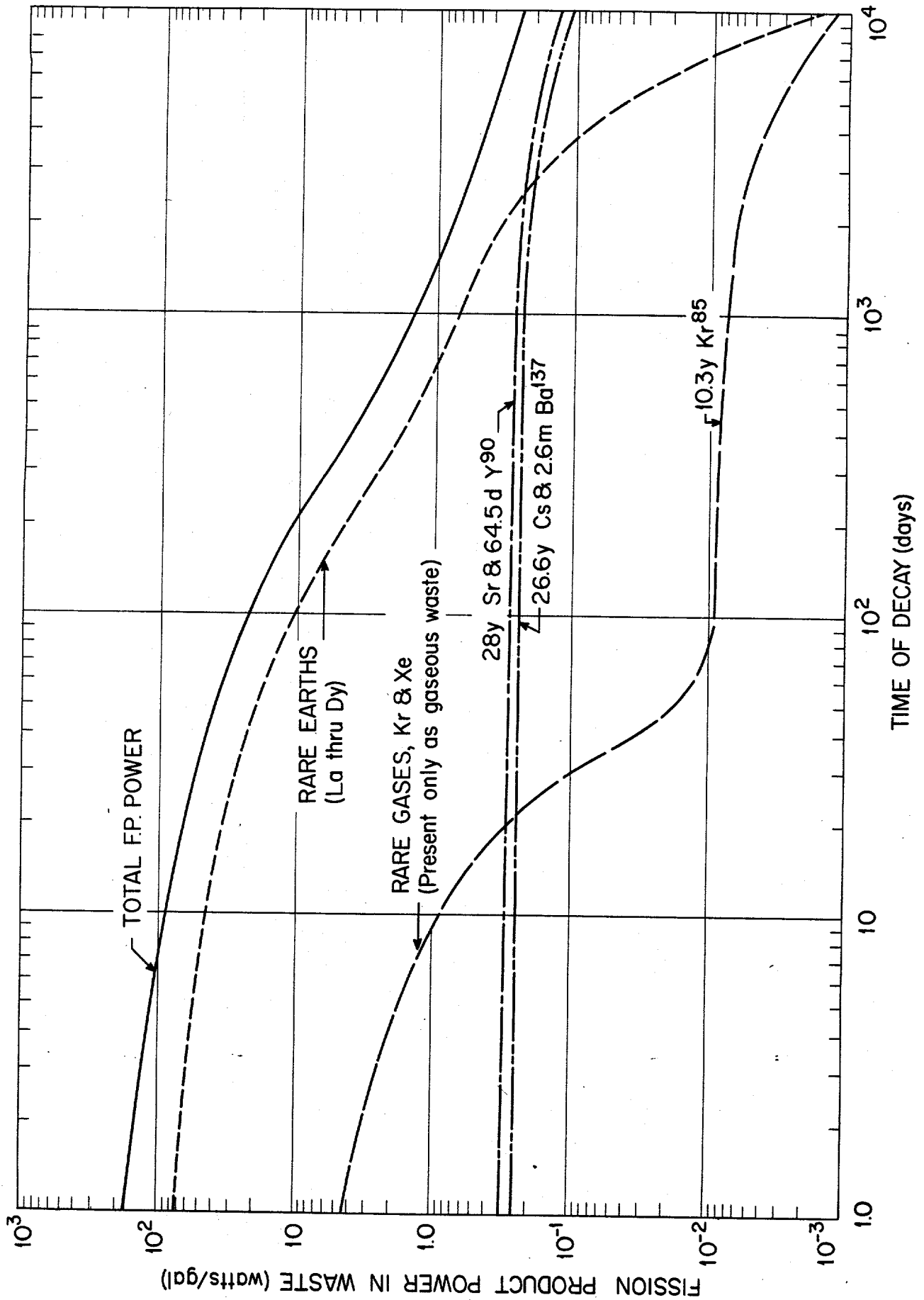


FIGURE 3 FISSION PRODUCT POWER IN WASTE AS A FUNCTION OF DECAY TIME. BASIS: 800 GAL WASTE PER METRIC TON U, IRRADIATED 10,000 Mwd/ton At 33 Mw/ton SPECIFIC POWER.

In this figure the specific fission product power (in watts/gal of waste) is plotted against the time of decay. It is assumed that 800 gal of waste has been produced from processing 1 metric ton of natural uranium, irradiated to 10,000 Mwd/ton at a specific power of 33 Mw/ton. Besides the total power, the contributions are noted for the rare gas fission products (normally separated when the fuel is dissolved), the rare earths, which are the major heat producers, and the long-lived hazards, Cs^{137} and Sr^{90} . After one day's decay, the fission power is rather formidable, 170 watts/gal; but after a 100 days' decay, a reasonable time to alloy before processing this fuel, the power has dropped to about 20 watts/gal. The power emission continues to fall until a decay time of about 3300 days, or nine years, the rare earths have begun to drop to a level where strontium and cesium and their daughters constitute the main source of power evolved in the waste. At this point the total power amounts to about 0.5 watt/gal and decreases according to the 27 to 28-year half-life of Sr^{90} and Cs^{137} .

Conclusion

This paper is concerned with the characterization of high-activity wastes from aqueous processing of irradiated reactor fuels. Characterization has been attempted on the basis of defining the major constituents present. Although the gross chemical and physical behavior of radioactive wastes may be controlled by the inert chemicals that predominate, it must be recognized that the hazards associated with the wastes are attributable to the fission products and the heavy elements which are present in relatively minute chemical concentrations. One approach to disposal is through chemical treatment designed to separate and concentrate the most hazardous of these isotopes. For effective hazard reduction, separations by factors of 10^6 and 10^7 would have to be attained, and the detailed chemistry of specific wastes would have to be understood and interpreted to a much greater degree than it has been possible to attempt here.

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